Establishing Measurement Traceability for Gaseous Mercury Emissions Monitoring

NIST was tasked with providing traceability for measurements of gas phase mercury (Hg^0) for U.S. Environmental Protection Agency (EPA) compliance purposes. On March 15, 2005 the EPA issued the Clean Air Mercury Rule (CAMR) that included a market-based cap and trade program. When the program is implemented the nationwide reduction in utility emissions of mercury will be in two phases. Mercury is a neurotoxin that accumulates in the food chain and is therefore a health concern. Concentrations of mercury in the air are of little direct health concern. However, when the mercury in the air re-deposits, it enters the food chain through bioaccumulation. Fish can have mercury levels several orders of magnitude greater than the level found in air. We are presently focusing our effort on developing standards for elemental mercury. The two sources of elemental mercury being considered as standards are gas cylinders and mercury vapor pressure gas generators. The objective is to certify a set of standard gas mixtures of mercury vapor in gas cylinders and to evaluate systems that generate and measure mercury vapor mixtures.

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Inductively coupled plasma mass spectrometry (ICP-MS) was used for the analyses of mercury in the gas phase. This technique had been used for many years at NIST for measuring mercury and certifying Standard Reference Materials in both solid and liquid matrices. Isotope dilution (ID) ICP-MS is a high-accuracy analytical technique, and was modified and evaluated as a viable method to be used for measuring mercury in the gas phase. NIST had analyzed mixtures of mercury vapor in nitrogen contained in high-pressure aluminum cylinders by trapping the mercury vapor on gold tubes and subsequently analyzing them using a cold vapor atomic absorption (CVAA) instrument. NIST had also investigated a system that could continually generate mercury in nitrogen mixtures at multiple discrete concentrations that could be user selected. Since ICP-MS isotope dilution has the potential of higher accuracy and precision, it was also investigated as a means of reducing the measurement uncertainty relative to the CVAA method.

NIST worked with a commercial specialty gas vendor to procure three sets of gas mixtures of mercury (Hg^0) in nitrogen. The nominal concentrations of the Hg^0 in the cylinders are 2 $\mu g/m^3$, 5 $\mu g/m^3$, and 20 $\mu g/m^3$. NIST also has access to two Hg^0 mixture generators capable of producing mixtures at the same concentration levels as the cylinders. NIST delivered three cylinders of mercury in nitrogen to the EPA with concentrations certified and traceable to the SI (International System of Units) by CVAA using a gold amalgam trap, and ID-CV-ICP-MS. While seeking traceable standards in the 2% relative uncertainty range, NIST has moved from CVAA (uncertainties in the 6% relative range) to ID-CV-ICP-MS as the primary reference method for mercury traceability.

Gases from the three gas cylinders maintained by NIST and the two Hg^0 vapor generators were analyzed using ID-CV-ICP-MS. With this method a known amount of a ^{201}Hg spike was generated from a primary standard solution with tin (II) chloride. For this demonstration of principle a 100% conversion rate was assumed for the stannous chloride reaction. The spiked gas stream was quantitatively mixed with the output from the gas cylinders or the gas generators before being introduced to the CV-ICP-MS instrument. The gas samples were originally analyzed using a gold amalgam mercury analyzer (CVAA). The average agreement between the two methods was 6% relative which is the estimated uncertainty in the CVAA measurements.

Two mercury generators were tested at discreet output concentrations over a range from 2 $\mu g/m^3$ to 60 $\mu g/m^3$. The output of the first generator was measured to be an average of 15% higher than the set point. The output of the second generator was measured to be within 1% of the set point at each concentration tested. The expanded uncertainties of the measurements are 1.87 % relative and are within the 2 % targeted goal.

NIST developed an isotope dilution/cold vapor/inductively coupled mass spectrometric method for measuring mercury vapor. This method provides the accuracy and precision required to support industry in its compliance with the EPA Clean Air Mercury Rule and its market-based cap and trade program.

Impact: EPA is using the certified cylinder mixtures in their program to audit mercury-monitoring sites to determine compliance with regulations. The cylinders have both an initial and a stability study concentration value assignment versus two NIST measurement systems. The program also provided data on the performance of mercury generation devices, and data showed that at least one of these devices is a viable alternate option for calibration and audit of mercury monitors.

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Future Plans: The cylinders containing the mercury mixtures are re-analyzed on a periodic basis to determine whether or not there is any degradation of the Hg^0 concentration. Development work has already begun on a method for studying mercury (Hg^{++}) to provide traceability for measurements being made in support of EPA's proposed regulations. The ICP-MS measurement system is to be characterized further in an attempt to reduce the uncertainty of the measurements